

SECONDARY RADIOACTIVITY
IN THE
ELECTROLYSIS OF THORIUM SOLUTIONS

BY
GEORGE B. PEGRAM.

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF
PURE SCIENCE, COLUMBIA UNIVERSITY

(Reprinted from the PHYSICAL REVIEW, Vol. XVII., No. 6, December, 1903.)

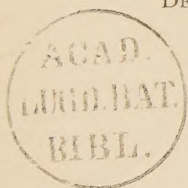
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IT being a well-known fact, studied especially by Rutherford and Soddy,¹ that the surface of bodies in the air near thorium compounds becomes charged with a temporary radioactivity under the influence of the thorium emanation, and that this activity is much increased if the surface is negatively electrified, it seemed probable that some interesting results might be obtained in connection with the electrolysis of solutions containing salts of thorium. Accordingly solutions of thorium nitrate were subjected to electrolysis, the electrodes being of platinum, with the general result that the anode became more or less radioactive. This radioactivity was only temporary, in some cases decaying at the rate of half its intensity in eleven hours, in other cases much more rapidly. The secondary activity due to the emanation from dry thorium oxide decays at the rate of half its value in about eleven hours, according to Rutherford.

The thorium salt used in most of the experiments was a so-called chemically pure thorium nitrate, prepared from Brazilian monazite by E. de Haen, of Hanover, and sold by the firm of Eimer and Amend, of this city. When not otherwise specified this is the thorium nitrate referred to throughout the paper. From solutions of this salt an adherent anode deposit varying in amount from a slight tarnishing of the platinum to a reddish brown or sometimes brassy colored coating was obtained. This coating was found to be highly radioactive. Some comparisons between its activity and that of metallic uranium showed that mass for mass it was at least 2,000 times as active as the uranium. It has been examined chemically by Professor W. H. Pegram, of Trinity College, N. C., who

¹ Phil. Mag., Jan., 1900, p. 1, Feb., 1900, p. 161, Sept., 1902, Nov., 1902, Jan., 1903, April, 1903, May, 1903.

found it to be lead peroxide. The presence of this matter which is deposited on the anode proves the impurity of the thorium nitrate, but the phenomena are none the less interesting.

If a solution of very pure thorium nitrate is used for electrolysis very little matter is deposited on the anode and the resulting activity of the anode is comparatively small. Three samples of especially purified thorium nitrate were very kindly furnished me by some chemist friends, Mr. Neish of our department of chemistry, Professor Baskerville of the University of North Carolina, and Mr. Whitaker, chemist of the Welsbach Gas Mantle Company. From none of these could any visible deposit be obtained on the anode, yet after electrolysis for considerable periods the anodes showed a certain amount of activity, though small in comparison to that of the deposit from the de Haen thorium nitrate and differing from it in its rate of decay.

If to a solution of pure thorium nitrate is added a small amount of some salt such as lead nitrate or copper nitrate, a metallic kathode or oxide anode deposit may be obtained, and such deposits are found to be radioactive.

One might expect that the kathode in electrolysis would collect a larger amount of radioactivity than the anode, since in the air near thorium compounds a negatively charged body, or kathode, becomes more active than an uncharged or positively charged body. Such is not the case in the electrolysis of thorium solutions. A small amount of thorium hydrate is generally deposited on the kathode during the electrolysis, but the temporary activity so noticeable on the anode is not present on the kathode. Since the thorium hydrate deposit can only be removed from the kathode by such treatment as would also remove the secondary activity if present, the kathodes tested for radioactivity were simply washed after the electrolysis and their activity tested at intervals over a period of several days, during which time no change could be detected in their activity, from which it is inferred that the total activity was due to the constant activity of the thorium hydrate. If a very heavy current density is used in the electrolysis the thorium hydrate comes down at the kathode as a somewhat gelatinous precipitate, which is redissolved on standing by the nitric acid from the anode.

The present paper is then an account of a number of experiments in connection with the radioactivity of the peroxide of lead deposit from the de Haen thorium nitrate solutions, of the anodes used in pure thorium nitrate solutions, of the anode and kathode deposits from salts introduced into the thorium solutions, of the gases liberated by electrolysis, and some other related matters. A previous short paper on the subject was read by title at the Pittsburg meeting of the American Physical Society, June, 1902, and an abstract printed in *Science*, November 21, 1902, p. 825. Other experimenters who have subjected radioactive solutions to electrolysis have been Dorn,¹ who found that on the electrolysis of solutions both the anode and kathode become temporarily radioactive, the anode more strongly so; Sella, who electrolyzed thorium solutions and found both anode and kathode temporarily radioactive; and Marckwald, who has obtained a new radioactive substance resembling tellurium by the electrolysis of solutions of polonium.

Apparatus. — Electrolysis of the thorium solutions was generally performed in a straight-walled glass beaker, 6 cm. in diameter. For anodes hollow cylinders of platinum, 8 cm. long, 1 cm. diameter, were used, the open lower end resting on the bottom of the beaker, so that the inside of the cylinder should take no part in the action. A sheet platinum kathode, just fitting inside the beaker, was used, the anode being placed in the middle of the beaker. With 100 c.c. of solution 3.5 cm. of the anode was immersed, giving an anode surface of 11 cm². Current was obtained from the 115-volt lighting circuit, resistance being introduced into the circuit to regulate the amount of current. The current was measured by a voltmeter, graduated in thirtieths of a volt, across a 5-ohm resistance in series with the electrolytic cell. Low voltage current was obtained by shunting the electrolytic cell with a variable resistance. The voltage of the circuit was fairly constant, so that the variations of current were within the errors of measurement of the radioactivity. Immediately after use in the electrolysis the anode was always washed under a stream of water and quickly dried in a current of air before testing its radioactivity.

¹ Ueber die von radioaktiven Substanzen ausgehenden emanation, *Abh. d. naturf. Ges. Halle*, 1900.

The radioactivity of the anode was measured by the conductivity it imparted to the air in a testing vessel, consisting of a metal cylinder 13 cm. high, 10 cm. in diameter, with removable lid, standing on a hard-rubber base. A brass rod, over which the cylindrical anode could be slipped, stood up through the middle of the base, below which it was connected to one pair of quadrants of an electrometer, the end of the rod below the hard-rubber base, and the short wire leading to the electrometer being surrounded by a grounded metal tube. This rod, and therefore the electrometer

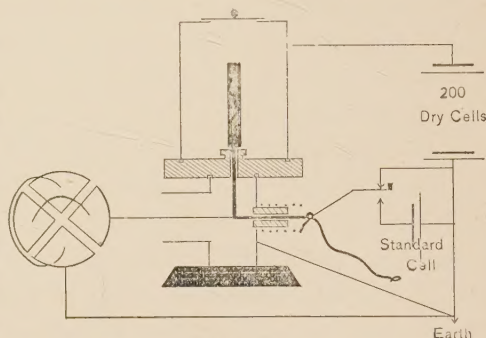


Fig. 1.

quadrants, was ordinarily grounded through a spring contact piece, but a slight pull on a string served to break the contact. The metal cylinder was connected to the negative pole of a battery of 200 dry cells (280 volts). When a radioactive anode is slipped over the central rod, the air in the vessel is ionized by the radiations and conduction takes place across the air column, thereby causing the electrometer needle to move at a rate proportional to the current. The voltage used was sufficient to utilize practically the total conductivity of the air column, and thus to obtain the maximum current. It has been shown¹ that under these conditions the current between the cylinder and central rod is very nearly proportional to radioactivity of the surface of the central rod.

The electrometer used is of the Dolezalek² quartz fiber suspension type, constructed in the department shop. Amber insulation, which is excellent even in comparatively damp air, supports the quadrants. The needle is of hard rolled aluminum foil .001 inch thick, of the Maxwell pattern and 3.8 cm. long. The use of a single piece of aluminum has some obvious advantages over the double thickness gilt paper needle of Dolezalek, especially as to

¹ E. Rutherford, *Phil. Mag.*, February, 1900.

² *Zeit. fur Inst.*, December, p. 345, 1901.

lightness and permanence of form under varying hygrometric conditions, though the damping is not quite as great as with the paper needle. The needle was charged by being kept in connection through the suspending quartz fiber, which had been dipped in a solution of calcium chloride, with the negative pole of a battery of 100 dry cells (140 volts), and at this voltage usually gave a deflection of 360 mm. divisions on a scale 130 cm. away when a Clark cell was connected in between the quadrants. The Clark cell could be thrown in by simply pressing a key and was used not only for checking up the sensitiveness of the electrometer, but also for quickly bringing the needle to rest at zero after a reading, since the suspended system was not quite dead-beat. The electrometer has been used for weeks without changing its sensitiveness more than 2 or 3 out of 360 divisions. Sometimes the electrometer had to be moved and then its sensitiveness changed, so that all the measurements which are compared with one another are reduced to the same electrometer sensitiveness by applying the ratio of sensitiveness on the two occasions as determined by the Clark cell, which gives a result very nearly correct, though it is true that the changes of sensitiveness to difference of potential and of sensitiveness to quantity of charge do not necessarily take place in the same ratio. In some of the measurements it was necessary to decrease the sensitiveness of the electrometer very much, and to do this a small leyden jar, capacity .0005 microfarad, was connected to the electrometer and testing vessel. This decreased the rate of movement of the needle with a given current to .115 of its rate without the jar attached, so the capacity of the testing vessel and electrometer is $.627 \times 10^{-4}$ microfarad. With the usual sensitiveness of 360 divisions to 1.43 volts a rate of 1 division per second corresponds to a current of 2.5×10^{-13} ampere through the testing vessel. There was always a small leakage from the testing cylinder to the electrometer, usually amounting to .13 division per second. It was quite constant and has been allowed for in the results when appreciably affecting them.

The Radiations from the Anode Deposit. — The secondarily active deposit gives off radiations chiefly of the non-penetrating α^1 type, with a small proportion of a more penetrating type, as is shown by

¹ Rutherford, Phil. Mag., January, 1899.

the absorption of the radiations by different thicknesses of aluminum. At the same time a radioactive gas similar to the thorium emanation is given off, which remains in the air of the testing vessel, giving it considerable conductivity for a few minutes after the active anode is taken out of the testing vessel. The conductivity is proved to be due to a radioactive substance in the air inside the testing vessel by the fact that when the air is blown out of the testing vessel the conductivity immediately drops to zero.

The following measurements made on an anode made quite radioactive show the penetrating power of the radiations through aluminum. The aluminum was in the form of cylinders of foil fitting closely around the radioactive anode. When no foil was used the conductivity of the air column, with this particular anode, was too great to measure without changing the electrometer arrangements, so a cylinder of lead with a longitudinal slit to expose one fifteenth of the active surface, was put over the anode and the resulting electrometer rate multiplied by 15.

Anode with Radioactive Coating from the de Haen Thorium Nitrate.

No. Thicknesses of Al. Foil, .04 mm. Thick.	Electrometer Divisions per Sec.
0	4,000
1	417
2	41
4	24
7	19
11	18
15	12

The question whether or not the ratio of radioactivity to mass of the lead peroxide deposit was constant during all stages of the electrolysis was investigated by using successive anodes in the solution for definite periods of time, and testing their activity, after which the deposit was dissolved off and the loss of weight determined. The balance used was sensitive to $\frac{1}{10}$ mg., but this of course did not enable a very accurate measurement of the mass of the deposit to be made, since the total mass was so small.

The small Leyden jar was connected to the electrometer during the measurements. Without it the number of divisions per second above would have been nearly nine times as great, too fast a rate to measure. It appears from the variation in the ratio of the activity to

Solution, 15 gm. thorium nitrate in 100 c.c. water. Current .84 ampere.

Anode Used.	Mass of Deposit.	Elec. Div. per Sec.	Ratio Activity to Mass.
First 20 minutes,	2.8 mg.	60	1.00
Next 20 "	2.1	43	.94
" 60 "	2.0	100	2.3
" 20 "	.3	13	2.0

the mass that the more slowly the matter is deposited the greater its activity.

The Effect of Continued Electrolysis.—The following results show how the activity of the anode when used in a solution of the de Haen thorium nitrate rapidly decreases with the duration of the electrolysis, due chiefly to the decreasing amount of the brown deposit on the anode. The experiment consisted in putting in fresh anodes at intervals as the electrolysis proceeded for periods of five minutes and testing the resulting radioactivity of the anodes.

Solution of 40 gm. $\text{Th}(\text{NO}_3)_4$ in 400 c.c. water. Current .44 ampere.

Duration of Electrolysis.	Activity of Anode, Electrometer Divs. per Sec.
5 minutes,	12.50
15 "	(50.00)
5 "	11.55
35 "	
5 "	6.25
35 "	
5 "	2.70
75 "	
5 "	1.62
365 "	
5 "	1.25

Thus by 475 minutes' electrolysis with the current strength as above the power of the solution to deposit radioactive matter on the anode had decreased to one tenth of its original amount. No doubt if the solution could be kept perfectly neutral the lead peroxide would come down faster, for the presence of free nitric acid around the anode tends to keep it in solution. After long electrolysis, when there is no longer any visible amount of matter deposited on the anode, the solution reaches a condition in which the power of depositing radioactive matter on the anode suffers little or no further decrease. The amount of activity gained by an anode from such a solution is

comparable to that obtained from the purest thorium solutions, so that it represents perhaps a deposition of radioactive matter unmixed with any ordinary matter from the solution.

It seemed probable that the radiations from the thorium salt itself might be changed in quality or quantity after being in a solution subject to electrolysis. The oxide being more convenient to work with than the nitrate, 100 mg. thorium oxide was prepared from the nitrate by heating it to a low red heat, and also 100 mg. from nitrate from a solution that had undergone long electrolysis, until very little radioactive matter was being deposited on the anode. The activity of the two samples of oxide was practically the same in amount, but the oxide from the nitrate that had been in the solution seemed to give off a slightly smaller amount of the radioactive emanation.

Activity of Anode as Related to the Amount of Thorium Salt.—The activity of the anode depends, other conditions being the same, on the total mass of the thorium nitrate used in the solution, except when dilute solutions, less than 2 gm. to 100 c.c., are used. Solutions of 100 c.c. water with different amounts of thorium nitrate were made up and subjected to electrolysis with equal currents for equal times and the activity of the anodes tested.

Time of electrolysis in each case five minutes. Current .44 ampere.

Solution.			Activity of Anode, Electrometer Divs. per Sec.
1.25 gm.	Th(NO ₃)	in 100 c.c. water.	1.85
2.50	"	"	3.03
5.00	"	"	6.45
10.00	"	"	15.8
20.00	"	"	31.3

With the exception of the first and weakest solution the activity increases pretty regularly with the amount of thorium salt in solution. Other experiments with dilute solutions showed considerable irregularity in the results.

If we keep the total mass of thorium nitrate constant, but vary the concentration of the solution by increasing the volume of water, not much difference is found in the activity of the anode. From 2.5 gm. thorium nitrate in 100 c.c. water, the anode gave 3.03

electrometer divisions per second, from 2.5 gm. in 200 c.c. water, the rate was 3.80 divisions per second.

The area of the anode in the solution, or in other words the current density at the anode, has considerable influence on the amount of activity. With 1 cm. of anode immersed in a certain solution, current .44 ampere, the activity was such as to give an electrometer rate of 2.70 divisions per second; with 7 cm. immersed in a similar solution the rate given was 4.16.

Activity as Related to Duration of Electrolysis and Current Strength.—As was expected the ratio of the activity of an anode to the time it has been used in electrolysis is nearly constant, when that time is not so long as to produce a noticeable effect on the power of the solution to deposit radioactive matter. Anodes were used in the electrolysis of a 500 c.c. thorium nitrate solution for various time intervals. The ratio of the activity to the time ran as follows:

Time of Electrolysis.	Ratio Activity of Anode to Time.
2 minutes.	.83
4 "	1.00
6 "	1.05
8 "	1.04
10 "	1.01
12 "	1.05
14 "	1.11
16 "	1.11

The relation between the current density and the amount of radioactivity on the anode is seen from the following results: The reason for the decreasing efficiency of the stronger currents is no doubt due to the nitric acid becoming so concentrated at the anode that the deposition of the brown coating was hindered to some extent. If very heavy current densities were used the brown deposit was sometimes redissolved.

Current Density at Anode, Amperes per cm ² .	Ratio Current Density to Activity.
.017	1.00
.037	.89
.085	.87
.132	.69

With a voltage across the electrolytic cell just below that required to liberate oxygen and hydrogen at the electrodes lead peroxide is

not deposited and the amount of radioactive matter of any kind deposited on the anode is small. From a solution of 5 gm. thorium nitrate no visible deposit was obtained in three hours, and the anode when tested showed no radioactivity.

Since thorium oxide is all the time giving off an emanation which causes secondary radioactivity, the following experiment was tried. 6.5 gm. thorium oxide was ground fine in a mortar and shaken up with 100 c.c. water. This water, with the thorium oxide still present in it, was subjected to electrolysis for twenty minutes, current .44 ampere. No radioactivity could be detected on either the anode or kathode. This is in accord with the results of Rutherford,¹ who finds that the emanating power of thorium, and therefore its power of imparting secondary activity to the surface of bodies in the neighborhood is at a maximum when it is in solution.

The Oxygen and Hydrogen from Electrolysis. — The oxygen and hydrogen liberated in the electrolysis of a solution of 20 gm. thorium nitrate in 300 c.c. water were collected separately in tubes above the electrodes and led at will into a testing cylinder, on the way passing through plugs of glass wool and a calcium chloride drying tube. The testing vessel consisted of a cylinder of brass 21 cm. long, 6 cm. in diameter, closed at each end with a plug of hard rubber. Through a hole in one plug the gas was led in from the drying tube, while a hole in the other allowed it to escape after traversing the length of the cylinder. A brass rod fixed to one of the hard-rubber plugs passed down the middle of the cylinder nearly to the other end. This rod was connected to the electrometer and the cylinder to a source of potential, usually 280 volts. The current between the cylinder and central rod, as given by the electrometer rate, was taken as a measure of the radioactivity of the gas.

The volume of the collecting and drying tubes and connections was 95 c.c., so with a current of .84 amp. through the solution, giving .106 c.c. hydrogen per second, it took the gas so long to get from the electrode to the testing vessel that the radioactive matter present had lost nearly all its activity, and the electrometer rate was very small. When the current was increased to 3.2 amp., giving .403 c.c. hydrogen per second, and the hydrogen led into the

¹ Phil. Mag., April, 1903.

testing vessel, the electrometer rate became steady in about fifteen minutes at 2.40 divisions per second. As soon as the hydrogen tube was disconnected the current began to decrease in the manner indicated by the following figures.

Hydrogen from Electrolysis of Thorium Nitrate Solution in Testing Vessel.			
Hydrogen flowing at rate of .403 c.c. per sec.,	2.40	elec. divs.	per sec.
45 sec. after hydrogen flow was stopped,	1.60	"	" " "
60 " later,	.80	"	" " "
120 " "	.18	"	" " "

Thus the rate of decrease of activity is about half in sixty seconds, or the same as that observed for the ordinary emanation from thorium, which is doubtless the radioactive matter present in the hydrogen.

When the oxygen was lead into the testing vessel, the same current flowing as above, giving .202 c.c. oxygen per second, a steady electrometer rate was attained in a few minutes. Results similar to those given above for hydrogen were obtained.

Oxygen from Electrolysis of Thorium Nitrate in Testing Vessel.			
Oxygen flowing at the rate of .202 c.c. per second,	8.6	elec. divs.	per sec.
20 sec. after oxygen flow was stopped,	7.5	"	" " "
60 " later,	3.7		
60 " "	1.9		

The rate of decay is the same as in the case of the hydrogen. The amount of activity measured would have been less than half that in the case of the hydrogen even if the concentration of the radioactive emanation were the same in the two gases when first liberated, since it took the oxygen twice as long to get from the electrode to the testing vessel and the activity of the emanation was decreasing in the meanwhile.

To decide the question of whether the radioactive matter was present in the same concentration in the two gases when first coming up from the solution the current was reduced to half so as to give the same rate of flow of hydrogen as of oxygen in the experiment above, and the hydrogen again led into the testing vessel. Now the steady rate attained was 7.5 electrometer divisions, or 12 per cent. less than with the same rate of flow of oxygen. The current was then decreased to .84 amp. and the electrolysis continued.

After 3 hours the current was again increased to 3.2 amp. and the hydrogen led into the testing vessel. The electrometer rate became steady at 15.1 divisions per second, as against 24.0 divisions when the electrolysis was first begun. This decreasing amount of the radioactive emanation in the gas as the electrolysis proceeds is sufficient to account for the difference in the concentration of the radioactive matter in the two gases, since the electrolysis had been continued for thirty minutes between the time of the measurements on the oxygen and those on the hydrogen. It is therefore probable that the concentration of the radioactive matter in the two gases is the same when they first leave the solution.

Electrolysis of Very Pure Thorium Solutions.—A 100 c.c. solution of (5 g. of) especially purified thorium nitrate which I was able to obtain through the kindness of Professor Baskerville was subjected to electrolysis for 20 minutes with a current of .84 ampere. No deposit was visible on the anode or kathode. The anode when tested for radioactivity gave an electrometer rate of 6.2 divisions per second. It was left in the testing vessel and 12 hours later was found to have practically no radioactivity. This was rather surprising, as an anode from the de Haen thorium nitrate would have lost only a little over half its activity in this time. The solution was again subjected to electrolysis under the same conditions and the anode afterwards tested at intervals with the following results :

Anode from the Pure Thorium Nitrate Solution (Baskerville).				
Immediately after the electrolysis.		5.4	electrometer	divs. per sec.
75 minutes later.		2.5	"	" " "
70 " "	"	1.1	"	" " "
183 " "	"	.6	"	" " "
121 " "	"	.3	"	" " "

From this it appears that the rate of decay of the secondary radioactivity excited by thorium is not a definite quantity. The rate indicated above is about half in one hour, the rate heretofore observed half in about eleven hours. The same solution was again subjected to electrolysis and a repetition of the results obtained.

Deposition of Radioactive Metals and Oxides from Thorium Solutions.—As mentioned before, it appears that when any metal or oxide is deposited electrolytically from a solution which contains

thorium, such deposit possesses a temporary radioactivity. A few milligrams of copper nitrate were added to a solution of 5 gm. thorium nitrate in 100 c.c. water and a current sent through the solution, the current density being adjusted to give a bright adherent deposit of copper on the kathode. The voltage across the cell was 1.8. A clean but very thin coating of copper was obtained in five minutes and the activity of the copper coated kathode then tested.

Kathode Coated with Electrolytic Copper from a Thorium Solution.

5 minutes after end of electrolysis.	2.62 electrometer divs. per sec.
3 " later.	2.42
3 " "	1.82
6 " "	.83
2 " "	.58
7 " "	.14
200 " "	.00

Here the rate of decay is even more rapid than in the case of the anodes from the pure thorium nitrate, though the source of the activity is the same thorium salt which gives an anode deposit, the activity of which decays at the rate of one half its value in eleven hours.

To get a deposit of oxide on the anode .1 gm. of lead nitrate was added to a 100 c.c. solution of 5 gm. thorium nitrate, and the solution subjected to electrolysis for 15 minutes with a voltage of 2.10 across the cell. A thin adherent coating of lead oxide was obtained on the anode. The following results show the amount of its radioactivity and its rate of decay.

Anode Coated with Lead Oxide Deposited from a Thorium Solution.

3 minutes after electrolysis.	8.5 electrometer divs. per sec.
1 " later.	6.8
3 " "	4.0
4 " "	2.5
7 " "	1.8
32 " "	.6

This is another example of rapid decay of the secondary activity from thorium.

Precipitates from Thorium Solutions. — Precipitates formed chemically in a solution with thorium nitrate present are radioactive. Silver chloride being a convenient precipitate to handle, tests were made

of the rate of decay of its activity. About .1 gm. silver nitrate was added to a solution of 5 gm. thorium nitrate in 100 c.c. water. After the silver had been in the solution ten minutes it was precipitated out with the requisite amount of HCl, excess of acid being avoided. The precipitate of silver chloride was filtered out, dried over a water-bath, transferred to a small metal disc, and this set on the top of the central rod in the usual testing vessel. Measurements were taken at intervals.

Silver Chloride Precipitated from a Solution Containing Thorium.

8.5 minutes after precipitation.	26.8 electrometer divs. per sec.
30 " later.	19.0
60 " "	11.0
95 " "	4.5

A further study of such radioactive precipitates will doubtless prove of interest. One experiment relating to the effect of the precipitation on the radioactive properties of the solution itself was tried. About 1 gm. silver nitrate was added to a solution of 5 gm. thorium nitrate in 100 c.c. water and then the silver precipitated out with HCl. The solution was immediately subjected to electrolysis for five minutes with a current of .84 amp. and the activity of the anode tested.

Anode from Solution of Thorium Nitrate in which Silver Chloride had been Precipitated.

180 seconds after end of electrolysis.	7.4 electrometer divs. per sec.
100 " later.	1.1
40 " "	.4
60 " "	.1
60 " "	.0

Then a similar solution of thorium nitrate without the addition of the silver salt and HCl was electrolyzed, after .5 c.c. HNO_3 had been added to make the amount of free acid in the solution at least as great as in the other solution. The activity of the anode after five minutes' electrolysis, current .84 ampere was such as to give an electrometer rate of 8.0 div. per. sec., with the usual rate of decay for the activity of the anode deposit from this de Haen thorium nitrate.

The rates of decrease with the time in intensity of the radiations from the various secondarily active substances obtained from thorium solutions is shown graphically in Fig. 2 by the curves, which are

plotted, as far as possible, so that the ordinates, representing intensities of radiation, are the same at the start, that is, immediately after the electrolysis or precipitation. Curve *I* is plotted for the radiation from the lead peroxide deposit, and it is to be noted that its intensity increases at first in the same way as has been observed by Rutherford for the radiation from bodies made secondarily active by the thorium emanation, then it decreases in a geometrical pro-

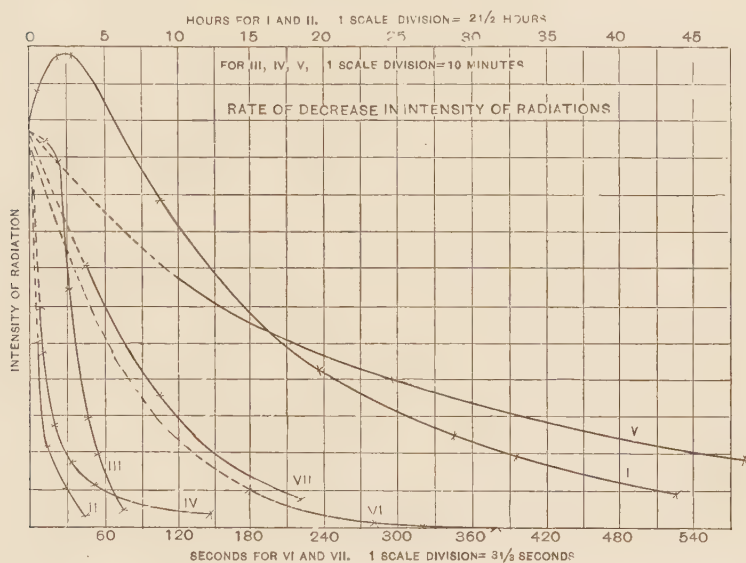


Fig. 2.

gression with the time, falling to half value in about eleven hours. If I_0 is the intensity at the beginning, and I the intensity at a time t later, we have $I = I_0 e^{-at}$, in which a may be determined from the fact that $I = \frac{1}{2} I_0$ when $t = 11$ hours. This decrease in approximately a geometrical progression with the time seems pretty general with secondary radioactivity. Curve *II* is plotted from the figures already given for the radiation from an anode after use in a very pure thorium nitrate solution, its decrease being about half in sixty minutes; *III* is for the radiation from copper deposited from a thorium nitrate solution, decrease half in seventy-five minutes; *IV* for that of lead oxide deposited similarly, decrease at first half in about sixty minutes; *V* for that of the silver chloride precipitated in

a thorium solution, decrease half in eighty minutes ; *VI* for that of the anode used in such a solution after the silver was precipitated, decrease half in forty seconds ; and *VII* for that of the active matter in the hydrogen from the electrolysis of a thorium nitrate solution, decrease half in one minute.

Summary. — In the electrolysis of solutions of the thorium nitrate prepared by de Haen, of Hanover, a deposit of lead peroxide is obtained on the anode, and this deposit is highly radioactive at first. The intensity of its radiations increases slightly for about two hours, then decreases, falling to half value in about eleven hours. The radiations consist chiefly, if not wholly, of the non-penetrating α type of radiations, with the exception that a small amount of radioactive gas similar to or identical with the thorium emanation is given off. The kathode has no secondarily active matter deposited on it.

The gases liberated in the electrolysis of a thorium nitrate solution are charged with radioactive matter, doubtless the ordinary emanation from thorium, which loses its activity at the rate of half in about one minute.

From solutions of the purest thorium nitrate obtainable no visible deposit is obtained on the anode, yet it is radioactive. The activity in this case decays rapidly, about half in one hour.

Anode and kathode deposits of oxides or metals from a solution containing thorium are radioactive. Their activity rapidly decreases, falling to half in a few minutes.

Precipitates thrown down chemically from solutions containing thorium nitrate are radioactive. Their activity also decays rapidly.

The secondary activity caused by thorium is not always the same in its rate of decay with time. The rate depends on how the secondarily active matter is separated from the thorium.

Coming to the question of the nature of the radioactivity shown by electrolytic and chemical deposits from thorium solutions, the lead peroxide, for example, two views are in general possible. First that the molecules or atoms of the lead peroxide have been so disturbed by being closely associated with the radioactive thorium that they now exhibit the properties of radioactive matter, or second, the radioactivity is a property of some kind of matter derived from the thorium which in some way becomes closely attached to the

lead peroxide. The second view of secondary radioactivity is strongly supported by most of the work relating to the question. Adopting it there is still the question of how the radioactive matter comes to be so closely connected to the lead peroxide as to be precipitated with it, is the connection an atomic, molecular, or simply mechanical one; and how does it come to exert an influence varying with circumstances on the rate of decay of activity of the radioactive matter? Experiments on the relation between the length of time the lead is present in the thorium solution and the amount of active matter it collects, also of the rate decay of the activity, easily suggest themselves and some of them at least would have been performed and the results given here, had not circumstances prevented the further use of the apparatus until the fall. We should expect no essential difference between the secondarily radioactive deposits obtained electrolytically and those obtained chemically, for the forces involved are of the same nature.

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